

[0001] The present ~~invention~~ application relates to a polyolefin with improved surface toughness, ~~especially in terms of~~ scratch resistance, and to a process for producing same. More specifically, the ~~invention~~ application relates to a polypropylene polymer ~~polyolefin on the basis of a polypropylene matrix material including~~ composition with bimodal rubber, ~~rubber compositions~~ as well as a process for producing said polymer ~~polyolefin~~ and ~~the use its use~~ as base in a mineral filled compound.

[0002] Various techniques for increasing the scratch resistance of polyolefin materials are previously known, ~~i.e. addition of silica materials~~. Thus, For example, JP 1318051 (Toray Silicone KK) discloses scratch resistant silica treated polyolefins ~~which for this purpose have been modified with a filler on silica basis~~. Said filler may have been surface treated with silane ~~type compounds~~.

[0003] JP 1104637 (Showa Denko KK) discloses scratch resistant polypropylene materials ~~on a polypropylene basis to which~~ that contain silica/alumina spheroids and ~~a polypropylene material functionalised~~ are functionalized with carboxylic acid or carboxylic anhydride ~~have been added~~.

[0004] U.S. Pat. No. 5,484,824 discloses a polypropylene composition containing ethylene-propylene rubber ~~which~~ that can be used for manufacturing exterior parts for automobiles.

[0005] U.S. Pat. No. 5,308,908 ~~refers to~~ describes a polypropylene resin composition comprising a specific mixture of ethylene/propylene and ~~other -olefin~~ other olefin copolymers for manufacturing car bumpers.

[0006] ~~A more recent application~~ EP-0804503 ~~of the present applicant~~ discloses that when a ~~functionalised~~ functionalized polypropylene material and an amorphous, fatty acid amide-modified silica gel are incorporated into certain polyolefin materials having a certain mineral

content, the scratch resistance of the material can substantially improved, ~~with retention of~~ while retaining the impact strength and the thermal shape stability (HDTA) of the material.

[0007] Though ~~said~~ the aforementioned materials show good scratch resistance properties, ~~properties these materials~~ they are based upon rather expensive filler systems i.e. surface treated fillers, which are rather expensive. ~~resulting in difficulty to penetrate the market due to the elevated price.~~

[0008] Conventional matrices like rubber modified R-TPO's and high crystalline heterophasic copolymers ~~are showing~~ show limited scratch resistance without ~~using any~~ using a modifier package, (~~e.g. HDPE,~~ e.g. HDPE, slip agents, high pigmentation, special talc quality) thus limiting the possibilities of using the materials in different applications, e.g. car interior, electrical appliances, where scratch resistance is an important property.

[0009] Accordingly, there is the need for polymer materials which show superior scratch resistance properties at reasonable costs.

[0010] On the basis of this situation, the inventors ~~of the present invention~~ have carried out intensive studies and found out that, amongst others, the following factors have an important positive effect on scratch resistance properties:

two rubber parts with highly differentiated Mw (IV) should be present in a polypropylene matrix, and

the low IV rubber must be ethylene rich.

[0011] By using this principle, the ethylene rich rubber particles are brought ~~more easily~~ towards the surface ~~layer in any moulded~~ a molded article. The ethylene rich rubber, including partly crystalline polyethylene, are more evenly distributed near the surface when compared to the

propylene rich rubber, ~~thus and by that~~ giving more stiffness/hardness to the ~~surface~~ surface, which improves the resistance to scratch damage.

[0012] A subsequent compounding step, if necessary, can be done without the addition of expensive, expensive treated fillers or excessive amounts of expensive elastomers, while still affording elastomers and still give elastomers with high scratch resistance ~~properties combined with the required~~ and the desired mechanical properties.

[0013] Furthermore, it was found out that the addition of an slip agent, e.g. erucamide, further improves the scratch resistance properties.

[0014] In a first aspect, the present ~~invention is therefore~~ application is directed to a process for ~~the preparation of~~ preparing a polypropylene polymer composition with bimodal rubber, said process comprising the steps of:

[0015] i) feeding propylene to a at least one slurry reactor and producing a polypropylene polymer matrix in the presence of a ~~polymerisation~~ polymerization catalyst in said at least one slurry reactor,

[0016] ii) transferring the slurry reactor product into a gas phase reactor (GPR),

[0017] iii) feeding a first mixture of ethylene and propylene to said first gas phase reactor and producing a first ethylene/propylene-copolymer in the polymer matrix in the presence of a ~~polymerisation~~ polymerization catalyst in said first gas phase reactor,

[0018] iv) transferring the first gas phase reactor product into a second gas phase reactor, and

[0019] v) feeding a second mixture of ethylene and propylene to said second gas phase reactor and producing a second ethylene/propylene-copolymer in the polymer matrix in the presence of a ~~polymerisation~~ polymerization catalyst in said second gas phase reactor,

[0020] vi) recovering the polymer product produced in step v) for further processing,

[0021] wherein said first and second ethylene/propylene mixtures having different composition ratios.

[0022] In a preferred embodiment, the ~~invention is directed to a process wherein the~~ composition ratios of said first and second ethylene/propylene mixtures are adjusted so that in the first gas phase reactor, a propylene rich EPR rubber is produced in the propylene polymer matrix, and in the second gas phase reactor, a ethylene rich EPR rubber is produced in the propylene polymer matrix.

[0023] In a further preferred embodiment, the propylene-rich EPR rubber has a higher molecular weight than said ethylene-rich EPR rubber.

[0024] The initial polypropylene polymer matrix will preferably be produced in a slurry reactor rather than in a gas phase reactor. The product of the slurry phase reaction is then preferably flashed to remove unreacted monomers and H<sub>2</sub> and transferred into a gas phase reactor where further reaction takes place with the formation of ethylene propylene rubber.

[0025] The polypropylene polymer matrix of the invention is produced preferably in at least one slurry reactor.

[0026] Suitable preparation methods will be readily determined by the person skilled in the art and include but are not limited to:

[0027] A. producing the polypropylene polymer matrix in a at least one slurry reactor, then feeding the flashed slurry reactor product into a gas phase reactor, and producing in a first gas phase reactor (GPR) the first ethylene/propylene-copolymer in the matrix, feeding the flashed first gas phase reactor product into a second gas phase reactor, and producing in the second gas phase reactor (GPR) the second ethylene/propylene-copolymer in the matrix.

[0028] B. producing the polypropylene polymer matrix in a at least one slurry reactor, as described in the first step of A, then feeding the flashed slurry reactor product into a gas phase reactor and then producing in said gas phase reactor (GPR) the first ethylene/propylene-copolymer in the matrix, flashing the gas phase reactor product and reintroducing the GPR product into the gas phase reactor, and producing the second ethylene/propylene-copolymer in the matrix in the gas phase reactor (GPR).

[0029] The monomer feeds into the various reactors may be adapted to produce a polymer with the desired properties and the amounts of monomers will be readily determined by the person after contemplating the present invention.

[0030] Preferably, a loop reactor is used as said slurry reactor although other reactor types such as a tank reactor could also be employed. According to another embodiment, said slurry phase is carried out in two slurry reactors, preferably but not necessarily in two loop reactors. In this way the supply/feeding speed to the GPR can be easily controlled. When continuing the ~~polymerisation~~ polymerization in the gas phase reactor or reactors, sufficient supply of the matrix propylene polymer can be established.

[0031] In the slurry reactor, propylene preferably acts not only as a monomer for ~~polymerisation~~ polymerization but also as a diluent. The slurry step, which preferably occurs in a loop reactor, is carried out by feeding into at least one slurry ~~polymerisation~~ polymerization step a reaction mixture containing 50-99.9 wt % of propylene up to 1 wt % hydrogen and a catalyst ~~system~~ system, whilst maintaining olefin ~~polymerisation~~ polymerization at a temperature below 75°C. Where two or more slurry reactors are used, these are preferably loop reactors and are fed by the same mixture as for a single slurry reactor.

[0032] Hydrogen may be added into either of the slurry phase or gas phase reactors to control the molecular weight of the respective polymer produced. The use of hydrogen in olefin ~~polymerisation~~ polymerization is conventional and will be readily applied by the person skilled in the art.

[0033] In the first gas phase reactor, the first gas phase ~~polymerisation~~ polymerization step is carried out by adding propylene and ethylene monomers where the resulting amount of C<sub>2</sub> in formed EPR range is between 39-74 mol %, preferably 53-65 mol %. If hydrogen is to be used in this stage, the molar C<sub>2</sub>/H<sub>2</sub> ratio should be between 0.01 to 0.1, preferably 0.03 to 0.06 and most preferably 0.05.

[0034] In the second gas phase reactor, the second gas phase ~~polymerisation~~ polymerization step is carried out by adding propylene and ethylene monomers where the resulting amount of C<sub>2</sub> in formed EPR ranges between 77-99.9 mol %, preferably 84-96 mol %. If hydrogen is to be used in this stage, the molar C<sub>2</sub>/H<sub>2</sub> ratio should be between 0.3 to 0.7, preferably 0.4 to 0.6 and most preferably 0.5.

[0035] The inventors ~~determined found out,~~ that carrying out the GPR ~~polymerisations~~ polymerizations in reversed order as explained before, the same results for the scratch resistance (SR) properties can be obtained. This proves the inventive concept of the invention that it is decisive for obtaining the desired SR characteristics, to prepare the rTPO with bimodal rubber on differing stages of the ~~polymerisation~~ polymerization process.

[0036] The slurry phase ~~polymerisation~~ polymerization may be carried out at temperatures of lower than 75°C., preferably 62-70°C. and pressures varying between 30-60 bar, preferably 30-50 bar. The ~~polymerisation~~ polymerization is preferably carried out in such conditions that 20-90

wt %, preferably 40-80 wt % from the polymer is ~~polymerised~~ polymerized in the slurry reactor or reactors.

[0037] The gas phase ~~polymerisation~~ polymerization step is carried out by transferring the reaction mixture from the slurry phase via a flashing unit for removing unreacted monomers and H<sub>2</sub>, preferably at pressures higher than 10 bars. The reaction temperature used will generally be in the range 60 to 115°C., preferably 70 to 90°C. The reactor pressure will be higher than 5 bars, and preferably be in the range 8 to 16 bar, and the residence time will generally be 0.1 to 0.5 hours.

[0038] ~~Polymerisation~~ Polymerization may be achieved using any standard olefin ~~polymerisation~~ polymerization catalyst and these are well known to the person skilled in the art. Preferred catalyst systems comprise an ordinary stereospecific Ziegler-Natta catalyst, metallocene catalysts and other organometallic or coordination catalysts. A particularly preferred catalyst system is a high yield Ziegler-Natta catalyst having a catalyst component, a cocatalyst component, and optionally an external donor. The catalyst system may thus contain a titanium compound and an electron-donor compound supported on an activated magnesium dichloride, a trialkylaluminium compound as activator and an electron donor compound.

[0039] A further preferred catalyst system is a metallocene catalyst having a bridged structure giving high stereoselectivity and which as an active complex ~~is impregnated~~ impregnated on a carrier.

[0040] Suitable catalyst systems are described in for example, FI Patent No. 88047, EP 491566, EP 586390 and WO98/12234 which are hereby incorporated by reference.

[0041] The amount of matrix component in the heterophasic copolymers of the invention is between 20 to 90%, preferably 60 to 90% and most preferably 65 to 70% by weight of the

heterophasic polymer. The amount of elastomeric copolymer prepared in the ethylene poor GPR polymerisation step may be in the range of 10 to 30%, preferably 15 to 25% and most preferably 18 to 22% by weight of the heterophasic polymer. The amount of elastomeric copolymer prepared in the ethylene rich GPR polymerisation step may be in the range of 5 to 20%, preferably 1.0 to 15% and most preferably 12 to 15% by weight of the heterophasic polymer. The elastomer components may comprise 95-5 wt %, preferably 95-20 wt % of crystalline phase and 5-95 wt %, preferably 5-80 wt % amorphous phase.

[0042] The xylene soluble fraction (XS) of the heterophasic copolymer is preferably in the range 3 to 35%, most preferably 6 to 20% by weight of the matrix component.

[0043] The propylene polymer matrix may also comprise any suitable ratio of monomers of propylene, ethylene and optionally other  $\alpha$ -olefin which results in an amorphous or semicrystalline/amorphous elastomeric copolymer, if desired. Preferably, the elastomeric component comprises a copolymer of ethylene and propylene only.

[0044] The polymer composition may be compounded with a mineral material to further enhance mechanical properties. Suitable minerals for use in the polyolefin alloy of the invention are finely divided minerals which might have been surface treated, e.g. silanized with one or more of the aminosilanes traditionally used for surface treatment of talc. Particularly suitable minerals ~~for use in the alloy~~ are wollastonite, kaolin, mica, calcium carbonate and talc, particularly talc. Preferably, the mineral has preferably a mean particle size D50 in the range of 0.5 to 10  $\mu\text{m}$ , more preferably 1-6  $\mu\text{m}$ .

[0045] The inventive polymer composition may further contain additives and fillers as usually used in the state of art and exemplified in the "Plastics Additives Handbook", Hanser Verlag Munich 2001.



[0046] The ~~inventive~~ polymer composition may further contain a slip agent which may contribute to the scratch resistance properties. Such slip agent may be selected from fatty acid amides, e.g. erucamide, oleamide, and high molecular weight polysiloxanes.

[0047] The targeted converting technique, but not limited to, is injection molding. ~~moulding~~.

[0048] The compounded polymer composition prepared according to the ~~inventive process~~ method disclosed herein can be used to replace ABS OR ABS/PC-made parts for electrical appliances, ~~where scratch resistance is an important property~~, car interiors and exteriors, in particular dashboards, door claddings, consoles, or bumpers, where improved SR properties are needed.

[0049] The invention is therefore also directed to those parts prepared by using the inventive composition.

## EXAMPLES

[0050] A combination of a slurry loop and 2 gas phase reactors were used for producing polypropylene copolymers ~~according to the invention~~.

[0051] The reactor product in powder shape has in itself a very good scratch resistance and can be used as such in applications where the mechanical properties are good enough. For many applications in the automotive and appliance area the stiffness requirement is higher, and therefore a mineral reinforcement is necessary. To reach a good distribution of the mineral in the PP a compounding step is needed. In this development the following additive package was used in the compounding step.

[0052] 75.9% reactor product

[0053] 0.1% CaSt

[0054] 0.2% Irganox B225

[0055] 0.3% GMS

[0056] 0.5% Erucamide

[0057] 3.0% dark grey ~~colour~~ color MB

[0058] 20% Talcum Luzenac A20 (D50 20 .mu.m)

[0059] The compounding extruder used was a Prism TSE 24 HC, twin screw extruder, (screw diameter, D=24 mm, total length=40D). ~~A drawing of the extruder can be seen~~

[0060] The polymer powder together with the additives was added through the main feeder and the 20% Talcum through the side feeder. The temperature setting in zone 1-10 and the die was the following.

[0061] 20, 200, 205, 210, 215, 215, 215, 215, 215, 210 and 210° C., which is a standard setting for compounding of PP.

[0062] For mechanical testing in ~~examples 1-5~~ examples 1-5, we have used injection ~~moulded~~ molded test bars, 80x10x4 mm and 60x60x3 mm. These test bars was produced on a Battenfeld 460 injection ~~moulding~~ molding machine, using standard temperature setting for PP.

[0063] Grained test plaques for scratch testing was made by injection ~~moulding~~ molding in a pre-grained mould with grains defined from GM called N111 (fine grain) and N127 (coarse grain). In addition a non-grained plaque was ~~moulded~~ molded for investigation of scratch depths.

[0064] The following analytical techniques were used in testing the polymers ~~synthesised~~:  
synthesized:

[0065] Melt flow rates (MFR) were measured under a load of 2.16 kg and at 230°C. according to ISO 1133.

[0066] Tensile strength (tensile stress at yield) was measured according to ISO 572-2 (cross head speed=50 mm/min).

[0067] Tensile modulus was measured according to ISO 572-2 (cross head speed=1 mm/min).

[0068] Flexural modulus was measured according to ISO 178.

[0069] Charpy, notched impact strength was measured according to ISO 179/1eA.

[0070] Vicat hardness was measured according to ISO306.

[0071] Fogging was measured according to DIN 75 201 B.

[0072] Carbon emissions was measured according to VDA277.

[0073] The scratch resistance was measured as explained below in more detail.

#### Scratch Resistance Test Method

[0074] As there is no uniform definition for scratch resistance, the inventors have searched for a uniformly applicable test method. Basically, a scratch is understood as a lasting deformation or wear of the surface of a material due to short term mechanical strain. Said scratch which is mainly depending on filler type and amount, surface texture, shape and force of indenter, surface hardness of polymer and smoothness of scratch bottom has to be examined re visibility (light scattering), area/size of deformation and depth. The inventors found out that using a specific testing device reliable and comparable results could be obtained.

[0075] Said test set up is based on a method from GM (GME 60280) equipped with a scratching device (Cross Hatch Cutter Model 420p, manufactured by Erichsen) for cutting a cross hatch (40x40 mm, distance between each grid line 2 mm) onto the specimen surface with different

grains (N 111---> fine grain/N127---> coarse grain). The instrument is equipped with a steel ball tip (0.5-3.0 mm). The cutting force is adjustable between 1 and 50N while the cutting speed is given by a simple mechanism (normally 1000 mm/min). Standard conditions used in the examples are based on 5N force, 1.0 mm tip and a cutting speed of 1000 mm/min.

[0076] With regard to a more objective scratch assessment, this method was selected instead of the conventional Erichsen tester (model 318) because of excluding the influence of the person performing the test.

[0077] Scratch evaluation was carried out by measuring the Delta L (dL) value by means of a spectrophotometer. This measurement corresponds to the difference in brightness of the treated resp. untreated polymer surface.

[0078] DeltaL>4: strong visibility of scratch

[0079] DeltaL<1: below this value significant lower visibility of scratch.

[0080] In addition a Scanning electron microscope and a laser confocal microscope was used to examine the topography and depth of the scratches.

## EXAMPLES 1-5

[0081] PP-matrix ~~polymerisations~~ polymerizations were carried out in a loop reactor. The matrix was produced in liquid propylene at 70°C. in the first stage. After the desired ~~polymerisation~~ polymerization time, the pressure was reduced slowly to 10.5 bar and ~~polymerisation~~ polymerization was continued in the gas phase reactor after flashing the matrix product. In the gas phase, semicrystalline and amorphous copolymers were ~~polymerised~~ polymerized at 80°C.

[0082] The catalyst used was prepared according to standard procedures, the activity of which was 40 kg PP/g cat h. The ~~polymerisation~~ polymerization conditions and the polymer properties are presented in Table 1.

#### Test Results

Run	IV split	C2 mol %	Total	MFR	Flexural	Charpy	Charpy
	GPR1/GPR2	GPR1/GPR2	Rubber	230°C	modulus	(+)23°C	(-)20°C
	(GPR2 = tot)	(GPR2 = tot)	(%)	Pellets	Mpa	KJ/m2	KJ/m2
1	1.63/3.22	12.2/21.1	28.9	9.8	798	60.2 (PB)	8.7 (B)
2	1.61/2.43	10.9/28.7	29.1	13.1	873	12.1 (B)	6.0 (B)
3	4.00/3.45	14.4/33.0	29.5	10.6	925	10.6 (B)	5.6 (B)
4	4.24/2.34	25.2/30.1	29.0	11.9	828	13.2 (B)	6.1 (B)
5	2.31/2.63	11.9/23.0	26.5	13.2	900	12.2 (B)	6.2 (B)

[0083] The compounds of Runs 1 to 5 were compounded with 20% talc (Luzenac A-20) and Erucamide and the scratch resistance of test samples has been examined.

Run	SR, dL	Ash	MFR	Flexural	Charpy	Charpy
	N111/ N127		230°C	modulus	(+)23°C.	(-)20°C.
			Pellets	Mpa	KJ/m2	KJ/m2
1-1	1.9/3.2	20.4	10.4	1786	27.2 (PB)	4.2 (B)
1-2	3.3/4.5	20.3	9.6	1832	25.9 (PB)	3.9 (B)
2	1.9/2.9	19.3	11.8	1915	6.7 (B)	2.4 (B)
3	0.8/1.3	20	11.2	1911	9.1 (HB)	2.3 (B)
4	1.8/2.9	20.9	10.9	1852	7.5 (HB)	2.4 (B)
5	0.94/1.7	20.3	12	1870	10.0 (HB)	2.6 (B).

\*) 1-2 is based on the same PP batch but with out ~~erucamide~~ erucamide, which proves an extra gain in SR may be obtained by adding the slip ~~agent in agent~~ to a PP with non-optimized ~~non optimised~~ EPR can be obtained.

[0084] As it can be seen ~~form~~ from the above ~~results~~ results, ~~of the studies of the inventors~~ the best scratch resistance performance can be obtained when combining a high C2 content with a low molecular weight IV. Comparing runs 3 and 5 lead to the results that the order of the differing GPR ~~polymerisation~~ polymerization reactions is not decisive for obtaining the desired SR properties as long as the molar ratios for C2 are maintained for the respective step.

[0085] If a higher impact strength will be needed the total rubber content should be increased and GPR split should be differentiated to yield more C3 rich rubber. For a higher stiffness, finer talc, a strong nucleating agent might be used and the C2 content should be maximized.

[0086] By using the inventive process, polymer materials can be obtained which have a dL value of preferably less than 4, and further improved values, when a slip agent, in particular erucamide is used, of even more preferably less than 2 dL<2.